HYDROGEN-CARBON MONOXIDE REACTIONS IN
LOW-RANK COAL LIQUEFACTION

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The primary role of the gas phase in low-rank coal liquefaction appears to be the stabilization of pyrolysis products from the coal via hydrogenation and, to a much lesser extent (in a non-catalytic system), hydrogenation of coal liquids. Hydrogen donor compounds and, to a lesser extent, the bulk of the solvent perform similar functions; that is to provide another source of hydrogen in addition to that in the gas phase to quench free radicals. Solvent effects will not be discussed in this paper. Carbon monoxide and water are the favored reactants over pure hydrogen at all temperatures from 350°C to 480°C for the liquefaction of low-rank coals. The amount of carbon monoxide consumed is dependent on the quantity of coal present, indicating that the driving force is the number of reactive sites initially present in the coal.

EXPERIMENTAL

Time Sampled Batch Autoclave

Studies on batch kinetics were carried out in a 1-liter, magnetically-stirred autoclave, which is outfitted to enable the charging of a slurry to the preheated reactor and for timed sampling of the gas and slurry phase during the course of an experiment. Hot charging brings the slurry to temperature in under 3 minutes, thereby eliminating the 1- to 2-hour heat-up associated with typical autoclave operation (1,2). Alternately, the slurry can be charged at an intermediate temperature and heated in stages to observe the effects of temperature change. An example of pressure, temperature, and gas composition data obtained where the autoclave was charged at room temperature and heated to reaction temperature is depicted in Figure 1. One thing to note is that the production of carbon dioxide and the consumption of carbon monoxide is kinetically rapid at temperatures above about 350°C. The experimental conditions for data reported in this paper are given in Table 1.

Coal

The coal utilized in the experiments was a lignite obtained from a mine located near Beulah, North Dakota (Sample B3). Proximate-ultimate data have been presented earlier (2). Lignitic coals are very reactive and are reported to evolve carbon dioxide at temperatures as low as 200°C (3). Dried lignites readily react with air and can spontaneously combust. Coal samples are therefore stored wet under nitrogen in lump form and pulverized just prior to use.

The B3 lignite sample was pyrolyzed in a stream of inert gas at 500°C by Timpe (4) at GFETC under an Associated Western University grant. The sample produced 0.17, 2.05, 14.92, 1.50, and 0.67 wt pct (MAF coal) of H_2, CO, CO_2, CH_4, and C_2-C_4 hydrocarbon gases, respectively. These data are in agreement with previously reported distillation assay data (5). In batch autoclave tests, the total gas discharged at the end of a run is slightly increased over the amount charged due to CO_2 production. For a charge of 3 moles of gas and 50 gm of MAF coal, a CO_2 concentration of about 5 mole pct is typical.

TABLE 1

Experimental Conditions for Reported Studies

| Figure-Curve | Run No. | Range of Temp. (°C) | Reactants Charged | | | | |
			CO_2 (moles)	H_2 (moles)	MAF Lignite (gm)	Solvent (gm)	Total H_2O (gm)
2,3	30	400-470	1.8	1.6	44	163	42
2,3	21	400-480	1.8	1.6	--	--	50
2,3	22	400-480	1.8	1.6	--	200	50
4-1	34	400-440	4.0	--	--	--	50
4-2	35	206-440	4.0	--	51	182	1
4-3	32	440	4.0	--	45	164	40
5-4	39-2	400-480	3.1	--	26	92	23
5-5	39-1	350-470	3.5	--	52	192	47
5-6	62	350-470	2.6	--	140	238	63

Lignitic coals also produce about 10 wt pct (MAF coal) of water during pyrolysis. This water was most probably bound as water of hydration (such as in clays or in humic acid structures)and would not be lost during drying at 110°C. This is potentially "inherent" water that could react with carbon monoxide via the shift reaction.

Solvent

The solvent used in the experiments was mainly a commercially obtained anthracene oil. In autoclave work the solvent was spiked with tetralin (about 7 wt pct of the slurry charged) to minimize coking during rapid heat-up. In the observed gas composition changes, the solvent primarily effects methane production (1). As will be discussed later, the solvent does not effect observed CO_2 or CO values and only slightly effects observed H_2 values.

Gas Analysis

Gas samples were analyzed by on-line GC, eliminating any air dilutions. The column used was a 12 to 14-ft, 1/4-inch 316 SS tube packed with Porapak QS. The GC was a Gow Mac maintained at 50°C employing argon as the carrier gas. Utilizing argon carrier gas results in high hydrogen sensitivity (0.02 mole pct), moderate sensitivity for CO_2 and CH_4 (0.1 to 0.3 mole pct), and poor sensitivity for propane (0.5 mole pct). Calibration gas and reactant gases were purchased pre-mixed from a local supplier.

The gas samples were removed from the gas phase of the autoclave. Previous data indicate that CO_2 and CH_4 are preferentially dissolved relative to H_2 and CO (1) in the liquid phase. Ratios of the mole pct of H_2, CO, CO_2, and CH_4 dissolved in the slurry to those in the gas phase were 0.87, 0.74, 1.38, and 1.10, respectively, at 435°C and 4500 psi. However, the value of dissolved gas was 37 ml (STP)/gm slurry; about 0.3 moles for a 200-gm charge, which was an order of magnitude less than in the gas phase, assuming all of the solvent was in the slurry phase. For the solvent in these tests, 40 to 60 pct was in the gas phase; therefore, there would be only about 0.1 to 0.2 moles of dissolved gas, which would have little effect on the composition of the analyzed gas phase. The moles of gas charged plus the moles of methane produced were found to be equal to the moles of gas metered from the autoclave at the end of an experiment plus the gas lost during sampling. Only special experiments enabled the observation of the direct production of CO_2 from lignite. In most cases the moles of CO charged equaled the moles of CO_2 and CO at the end of an experiment.

RESULTS

Experiments have been made to determine how CO and CO-hydrogen interact with the reactor walls, water, solvent, wet coal, and dry coal.

In Runs 21, 22, and 30, H_2-CO (50:50 wt pct) was reacted with water, water-solvent, and water-solvent-coal, respectively, in temperature-stepped experiments. The changes in the gas phase concentrations of CO and H_2 are depicted in Figures 2 and 3. For water and water-oil systems (Fig. 2), CO is slowly consumed only at temperatures above 400°C. Adding wet lignite dramatically increases the consumption of CO even at temperatures below 400°C. In the water-only experiments, the amount of CO consumed is the same as the amount of hydrogen produced. However, in water-oil and in water-oil-coal systems, a slight hydrogen decrease (note expanded scale) is observed (Fig. 3). In systems with oil or oil-coal present, some of the decrease is due to dilution (hydrocarbon gas production and/or the direct production of CO_2 from coal caused an increase of about 10 pct in the total gas in the reactor by the end of a run). As indicated by the data, slightly more H_2 appears to be consumed when coal is present in the oil. These data also illustrate that CO is preferentially reacted at all temperatures.

Figure 4 depicts data for reaction of CO with dry and wet coal-oil slurry. For comparison, data from Run 34 are shown where no coal or oil was present. Run 32 was a hot-charge experiment, which shows the rapid initial CO consumption when wet lignite is present. In Run 35, the lignite was dried in the solvent at 110°C with a nitrogen purge prior to charging. While Run 35 was a slow heat-up with temperature stepping (1 hr at 400°C and 1 hr at 440°C), CO consumption and CO_2 production were essentially complete when 400°C was reached, and very little hydrogen was produced.

The amount of CO consumed has also been found to be dependent on the amount of coal charged. Figure 5 depicts CO consumption when 26, 52, or 140 gms of MAF lignite were charged to the autoclave. For Run 62, where 140 gms were charged, over 95 pct of the CO charged was consumed. The shaded areas (the difference between the top and bottom lines) indicate the moles of H_2 observed versus time. When 140 gms of lignite was present, the amount of hydrogen observed was greatly reduced, indicating that a direct reaction with lignite to produce CO_2 is favored over reactions that would produce both CO_2 and H_2.

CONCLUSIONS

The data that have been presented support the following conclusions:

a) The shift reaction
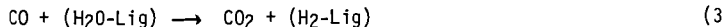
$$CO + H_2O \longrightarrow H_2 + CO_2 \tag{1}$$

is not catalyzed by the reactor walls or an aromatic solvent (Figs. 2 and 4). However the solvent does undergo some slow hydrogenation (Fig. 3).

b) The presence of lignite catalyzes the shift reaction, but a reaction such as

$$CO + (Oxy\text{-}Lig) \longrightarrow CO_2 + Lig' \tag{2}$$

or

$$CO + (H_2O\text{-}Lig) \longrightarrow CO_2 + (H_2\text{-}Lig) \tag{3}$$

is favored, especially at lower temperatures (Figs. 1 and 5).

c) The reported equilibrium values (6) for the shift reaction decrease with increasing temperature from 28.25 at 327°C to 6.3 at 527°C. In runs without lignite, the concentration of CO steadily decreases at all temperatures with time and is at all experimental times far from an equilibrium value. With coal present, the amount of CO consumed is directly dependent on the amount of coal charged. This indicates that the coal has a certain number of reactive sites and that when they have reacted, the reaction essentially stops. While the shift reaction is no doubt occurring, it does not appear to be the most important reaction, at least not in these experiments.

d) H_2 is produced via the shift reaction (Fig. 5) in $CO-H_2O$ systems. However, since its concentration does not increase when both H_2 and $CO-H_2O$ reactants are present (Fig. 3), hydrogen must be reacting. However, the net consumption of charged hydrogen is small compared to that of CO. Therefore, in competitive reactions CO reacts more rapidly than hydrogen.

The preceding statements re-emphasize the fact that CO undergoes reactions with lignite that are kinetically more favorable than those with hydrogen, and that these reactions are favorable throughout the temperature range studied (350-480°C).

LITERATURE CITED

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LIST OF FIGURES

Y-axis: CO REACTED, moles (0 to 2)

X-axis: TIME, hours (0 to 3)

Curve 3: CO + LIGNITE + H₂O
Curve 2: CO + DRY LIGNITE
Curve 1: CO + H₂O